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Summary of U.S. EPA Sponsored Large Chamber Characterizations of Emissions from Unvented Kerosene Space Heaters

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16. ABSTRACT The paper summarizes EPA-sponsored large-chamber characterizations from unvented kerosene space heaters. EPA's AEERL has been investigating emissions from kerosene space heaters since 1984. The focus of EPA's efforts has been on evaluating organic and particulate emissions from those sources and the development of emissions factors for these pollutants. To date, 26 makes and models of kerosene space heaters have been tested in the program. The tests have covered a variety of use conditions in different test environments, including hoods, chambers, a test house, and the "field." Objectives of the first study in 1984 were to determine the more appropriate method (i.e., hood vs. chamber) of evaluating emissions from kerosene heaters, and to characterize the organic and particulate emissions from two such units. This work concluded that, except for particulate measurements, the testing methods were basically the same for all pollutants. However, the larger volume of the chamber permitted particle formation similar to that anticipated to occur in indoor environments. Consequently, chambers were selected as the method of choice for further studies. Characterization continued during the 1985-86 heating season in an environmental test chamber. EPA's efforts to characterize indoor air pollution from kerosene space heaters were capped in 1988-89 in eight mobile homes.

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Space Heaters		13A
Combustion		21B
Organic Compounds		07C
Particles		14G

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A SUMMARY OF U.S. EPA SPONSORED LARGE CHAMBER CHARACTERIZATIONS OF EMISSIONS FROM UNVENTED KEROSENE SPACE HEATERS

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INTRODUCTION

Kerosene heaters are used as both supplemental and primary residential heating sources. It has been estimated that approximately 7 million unvented kerosene heaters were in use in the U.S. during the 1986-1987 heating season and that the present annual sales in the U.S. are probably on the order of 825,000 units, down from the 2-3 million units per year in the early 1970s (ref 1). The U.S. EPA's Air and Energy Engineering Research Laboratory (AEERL) has been investigating emissions from kerosene space heaters since 1984. The focus of EPA's efforts has been on the evaluation of organic and particle emissions from these sources and the development of emissions factors for these pollutants. To date, 26 makes and models of kerosene space heaters have been tested in the program. The tests have covered a variety of use conditions in different test environments, including hoods, chambers, a test house, and the "field".

Testing was begun in 1984 at the Lawrence Berkeley Laboratory (LBL), Berkeley, CA. The objectives of this first study were to determine the more appropriate method (i.e., hood vs. chamber) of evaluating emissions from kerosene heaters, and to characterize the organic and particulate emissions from two such units. The LBL work concluded that, with the exception of particulate measurements, the testing methods were basically equivalent for all pollutants. However, the larger volume of the chamber permitted particle formation similar to that anticipated to occur in indoor environments. Consequently, chambers were selected as the method of choice for further studies.

Characterization was continued during the 1985-1986 heating season in the environmental test chamber at the J.B. Pierce (JBP) Foundation Laboratory, New Haven, CT. The JBP work was divided into two phases with the overall objective of further evaluating the particulate and organic emissions from kerosene heaters and determining the qualitative and quantitative impact that heater design, heater age, fuel changes, and operation and maintenance have on emissions.

EPA's effort to characterize potential indoor air pollution from kerosene heaters was capped in 1988-1989 by a field survey to measure kerosene heater emissions in eight mobile homes in two mobile home parks located near Research Triangle Park (RTP), NC. The survey involved three EPA components: AEERL, the Health Effects Research Laboratory (HERL), and the Atmospheric Research and Exposure Assessment Laboratory (AREAL). The objective of the survey was to determine the exposure of users to the pollutant mixture generated by kerosene heaters under typical operating conditions.

MATERIALS AND METHODS

The work at LBL consisted of two components (a hood and a chamber), both of which were conducted in LBL's 27 m^3 environmental chamber. The study provided a semi-quantitative analysis of the organic and particulate emissions from two heaters, a maltuned convective and well-tuned radiant heater. (The convective heater was maltuned to enhance particle generation.) A 1-K kerosene fuel (i.e., a kerosene with < 0.04% sulfur (S) by weight) was used in both components of the LBL study. The pollutant measurements were used in mass balance equations to develop pollutant emissions rates. A detailed description of the test methodology and data derived from the study have been published elsewhere (ref 2).

The JBP work was conducted in a 34 m^3 stainless steel environmental chamber. Phase I of the JBP work was screening using a 0.039% S fuel and 12 heaters loaned by the U.S. Consumer Product Safety Commission. Phase II of the JBP effort focused on potential fuel influences on acidic aerosol emissions from four additional kerosene space heaters. A 0.024% S fuel and a "superclean" 0.0018% S fuel were used in this portion of the study, and acid aerosol emissions were measured by two test methods: 1) collocated filters provided by Brookhaven National Laboratory, and 2) collocated Harvard/EPA Annular Denuders (HEADs). Pollutant source strengths and emission factors were also derived using mass balance equations. The methodology has been described in other publications (refs 3,4).

RESULTS AND DISCUSSION

Table 1 presents selected pollutant emission factor data taken from the combined Phase I and II JBP work. The data are grouped according to the fuel combusted for five kerosene heaters: radiant (R), radiant/radiant (R/R), convective (C), convective/radiant

(C/R), and wickless (W) (see Table 1).

Inorganic Combustion Gases

NO_x and SO_2 emission factors are currently available for only the 0.039% S fuel type. Across all heaters tested, the individual NO_x emission factors ranged from 9.9 to 80.9 ug/kJ; the averaged emission factors ranged from 13.2 to 65.8 ug/kJ (see Table 1). For the fuels tested, the convective heaters produced on average 4 to 5 times more NO_x than the other designs. Those heaters incorporating a radiant feature (i.e., R, C/R, R/R) produced the lowest NO_x averages.

The individual SO_2 emission factors ranged from 5.1 to 15.3 ug/kJ; the averaged emission factors ranged from 5.1 to 13.5 ug/kJ (see Table 1). Although SO_2 emissions are reported to be independent of heater design, the R/R design was lower in SO_2 emissions by nearly a factor of 2 than the other heater types tested. It is believed that the emissions of SO_2 were affected by a manufacturer-installed catalytic device and, possibly, by increased particle formation due to a deteriorating wick. These conditions may have increased the conversion of SO_2 to $SO_4^=$ adding to the particle mass.

Gas-phase nitrogen based acids (i.e., HNO_3 and HNO_2) were produced by kerosene space heaters using both the 0.0018% S and the 0.039% S fuels. The average of the total acid gas emission factors ranged from 3.01 to 7.57 ug/g of fuel burned with the 0.024% S fuel and from 2.49 to 7.29 ug/g of fuel burned for the 0.0018% S fuel. With both fuels the total HNO_3 plus HNO_2 emissions are greatest for the W and the C designs, indicating a potential association of emissions with heater type. In R category, the arithmetic averages of the total acid emission factors for one heater burning three different fuels was: 2.67 ug/g (n=2), 0.0018% S; 3.96 ug/g (n=2), 0.024% S; and 4.85 ug/g (n=2), 0.039% S. This represents a 1.5 and 1.8 increase as fuel S increases from 0.0018% S to 0.024% S, and 0.039% S, respectively, indicating a potential fuel effect as fuel S increases. The HNO_3/HNO_2 ratios for the same R heater burning were: 34.6 (n=2), 0.0018% S; 11.35 (n=2), 0.024% S; and 11.42 (n=2), 0.039% S. This also indicates a potential fuel effect which favors the production of HNO_3 at very low levels of fuel sulfur.

Particles

Approximately 99% of the particles produced by kerosene space heaters are less than 2.0 um in diameter. The principal inorganic constituents of the aerosol particulate are sulfate and ammonium ions, accounting for 62 to 82% of the total particulate mass. The chemical form of the particulate, as determined by the equivalence ratios, is probably a mixture of acidic ammonium bisulfate and neutral ammonium sulfate. Free H^+ was detected in the initial JBP work indicating the presence of strong acid associated with the particle mass. The presence of free H^+ was also detected in JBP Phase II; however, it occurred randomly in both the 0.0018% S and the 0.024% S fuels.

The emission factor data clearly demonstrate the influence of fuel on particulate emissions

(see Table 1). In the R heater category, the R unit tested using all three fuels demonstrated a continuous increase in emissions factors, 6.3 ug/g (n=1), 11.6 ug/g (n=2) and 35.8 ug/g (n=2), as fuel sulfur content increased 0.0018% S, 0.024% S, and 0.039% S, respectively. The averaged emission factor for the individual heaters burning the 0.0018% S fuel ranged from 5.4 ug/g of fuel burned (n=2) in the C/R to 8.3 ug/g of fuel burned (n=2) in the W design. With the 0.024% S fuel, the averaged emission factors ranged from 11.6 ug/g of fuel burned (n=2) in the R to 17.5 ug/g of fuel burned (n=2) in the W design. In both cases the W design was the highest emitter. This represents an increase in emissions factor of 1.8, 2.3, 2.8, and 2.1 times for the R, C, C/R, and W designs, respectively, as the fuel S content increased from 0.0018% S to 0.024% S. (The R/R unit did not show a corresponding increase in the particulate emission factor; the reason for this is currently not known.)

Particle Bound and Semivolatile Organics

In reasonably maintained, well-operated kerosene heaters, the particulate is composed of 24 to 36% carbon of which 78 to 98% is organic carbon (ref 4). A chromatogram of the extractable carbon shows a strong similarity to the chromatogram of the kerosene fuel combusted to produce the particle indicating a an absorption of kerosene vapors on the particle surface. Both the LBL and the JBP work indicated that maltuned heaters produced greater quantities of particles than well-tuned heaters (ref 2). In the LBL work, increased particle production resulted in a variation in the mass distribution between the particle bound and the semivolatile organics; however, this did not cause a proportionate increase in extractable organics. The emission rates of total polycyclic aromatic hydrocarbons (PAHs) attached to particles ranged from 0.2 to 1.3 ug/h in two composited R heater samples, and was 180 ug/h in the single maltuned C heater composited sample. LBL work further identified several carcinogens including fluoranthene, indeno(c,d)pyrene, 3-nitrofluoranthene, and 1-nitropyrene on the particles (ref 1).

The composition of the semivolatile organics was semi-quantitatively determined in the LBL work (ref 2). For the R and the maltuned C heater in the LBL study, total PAH emission rates ranged from 59.3 to 250.2 ug/h for the composited R heater samples, and was 204 ug/h in the C heater composite. The classes of compounds represented by the largest emissions rates were the aliphatic hydrocarbons, aliphatic alcohols, phthalates, and hydronaphthalenes. These compounds are constituents of kerosene fuel and were present in quantities at least an order of magnitude greater than those organics derived from combustion. Two known mutagens, fluoranthene and 9-nitroanthracene, were also observed in the semivolatile fraction.

Vapor-Phase Organics

The vapor-phase organics are composed primarily of c-8 to c-15 alkanes, the source of which appears to be the evaporation of kerosene fuel. Other vapor-phase organics present include the c-13 alkanes which are probably the products of incomplete combustion. Emission factors for vapor-phase organics ranged from 20 to 230 ug/g of fuel burned.

Mutagenicity

The organic carbon component of the particulate consists of 22 to 77% extractable material. An analysis of the extracts indicates the presence of n-alkanes as well as PAHs and nitrated PAHs. All the particle samples assayed for mutagenicity showed dose-response activity in TA98 without metabolic activation with S9, indicating the presence of direct acting mutagens. In general, the particulate samples from C and R heaters showed the lowest mutagenic activity. The R heaters were low, ranging from 29.1 to 68 rev/m^3 of air sampled. The C heaters, however, showed a wider range of activity with a factor of 4 difference between the highest and the lowest. The C/R and the R/R heaters showed highest mutagenic activity, indicating that these designs may impact mutagenic activity more than the simple C or R designs.

CONCLUSIONS

Unvented kerosene space heaters are a source of a complex pollutant mixture which consists of both inorganic and organic components. NO_x is greatest for C heaters. SO_2 emission factors are dependent on the fuel selection; however, the relationship with heater type is not yet known. Gas-phase acids (i.e., HNO_2 and HNO_3) appear to be influenced by heater type with the C and W heaters being the largest producers. There also appears to be a fuel effect at very low sulfur levels on the formation of HNO_2 and HNO_3. Particle production appears to be strongly influenced by fuel sulfur and inçreases as fuel sulfur content increases; aerosol acidity does not appear to be so linked. Vapor-phase and particle bound organics are similar in composition to unburned kerosene.

REFERENCES

1. Barnes, J., Holland, P., and Mihlmester, P. Characterization of population and usage of unvented kerosene space heaters, EPA-600/7-90-004 (NTIS PB90-155573), January 1990.
2. Traynor, G.W, Apte, M.G, Sokol, H.A., and Chuang, J.C., Comparison of measurement techniques for quantifying selected organic emissions from kerosene space heaters, EPA-600/7-90-006 (NTIS PB90-187022), February 1990.
3. White, J.B., Leaderer, B.P., Boone, P.M., Hammond, S.K., and Mumford, J.L., Chamber studies characterizing organic emissions from kerosene space heaters, pp. 98-101, Proceedings of the 1987 EPA/APCA International Symposium: Measurements of Toxic and Related Air Pollutants, Research Triangle Park, NC, EPA-600/9-87-010 (NTIS PB88-113402), May 1987.
4. Boone, P.M., Leaderer, B.P., White, J.B., and Hammond, S.K., Chamber studies characterizing organic emissions from unvented kerosene space heaters: phase II, pp. 769-774, Proceedings of the 1988 EPA/APCA International Symposium: Measurements of Toxic and Related Air Pollutants, Research Triangle Park, NC, EPA-600/9-88-015, May 1988.

Table 1. Summary of Kerosene Heater Emission Factors

Heater Type	Pollutant range (Average) NO_x (ug/kJ)	SO_2 (ug/kJ)	HNO_2+HNO_3 (ug/g)	Particulate Mass (ug/g)	Fuel Type (% S)
R	9.9-17.4 (13.3,n=5)	7.8-15.3 (10.8,n=5)	4.64-5.05 (4.85,n=2)	33-202 (137,n=6)	0.039
	NA	NA	3.66-4.25 (3.96,n=2)	10.7-12.7 (11.6,n=2)	0.024
	NA	NA	2.33-3.01 (2.67,n=2)	6.3 (6.3,n=1)	0.0018
R/R	13.2 (13.2,n=1)	5.1 (5.1,n=1)	NA	175-260 (217.5,n=2)	0.039
	NA	NA	2.80-3.22 (3.01,n=2)	11.1-11.6 (11.4,n=2)	0.024
	NA	NA	2.18-2.79 (2.49,n=2)	11.9-14.3 (13.1,n=2)	0.0018
C	45.5-80.9 (65.8,n=3)	12.2-14.9 (13.5,n=3)	NA	20-59 (42, n=3)	0.039
	NA	NA	6.10-6.14 (6.12,n=2)	14.8-16.0 (15.4,n=2)	0.024
	NA	NA	4.27-4.64 (4.46,n=2)	5.6-7.9 (6.8, n=2)	0.0018
C/R	13.2-17.9 (15.5,n=3)	8.6-12.9 (10.2,n=3)	NA	27-54 (46.7,n=3)	0.039
	NA	NA	4.21-4.26 (4.24,n=2)	13.6-16.5 (15.1,n=2)	0.024
	NA	NA	2.54-2.81 (2.68,n=2)	4.9-5.8 (5.4,n=2)	0.0018
W	NA	NA	NA	NA	0.039
	NA	NA	7.50-7.64 (7.57,n=2)	15.8-19.2 (17.5,n=2)	0.024
	NA	NA	6.99-7.59 (7.29,n=2)	7.6-8.9 (8.3, n=2)	0.0018

NA-Not Available